

10/522308

PCT/GB 2003 / 002117

REC'D 507/PTO 25 JAN 2005

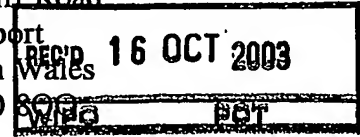
INVESTOR IN PEOPLE



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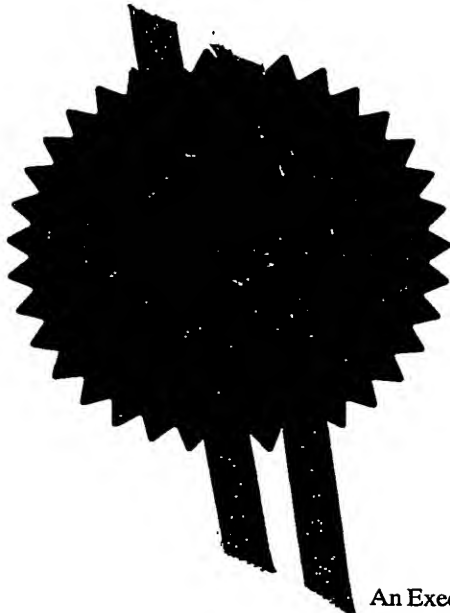


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Signed *Stephen Hordley*  
Dated 8 October 2003

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# Request for grant of a patent

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THE PATENT OFFICE

27 JUL 2002

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The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

1. Your reference

SMC 60531/GB/PI

2. Patent application number

(The Patent Office will fill in this part)

0217446.4

27 JUL 2002

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Avecia Limited  
Hexagon House  
Blackley  
Manchester, M9 8ZS  
United Kingdom

Patents ADP number (if you know it)

07764137001

If the applicant is a corporate body, give the country/state of its incorporation

GB

4. Title of the invention

COMPOSITION, USE AND PROCESS

5. Name of your agent (if you have one)

MAYALL, John

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Avecia Limited  
Hexagon House  
Blackley  
Manchester, M9 8ZS  
United Kingdom

Patents ADP number (if you know it)

6244313002 4

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or

c) any named applicant is a corporate body.  
See note (d))

# Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description

26

Claim(s)

04

Abstract

01

Drawing(s)



10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

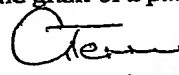
Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature



Date 25 July 2002

Avecia Limited Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Mrs K.M. Pinder/Miss G. Terry 0161 721 1361/2

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- For details of the fee and ways to pay please contact the Patent Office.

SMC 60531

APPLICANTS

Avecia Limited

TITLE

COMPOSITION, USE AND PROCESS

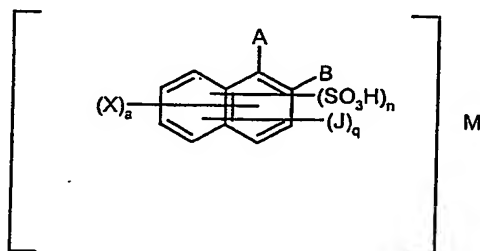
COMPOSITION, USE AND PROCESS

This invention relates to dyes, to inks and to their use in ink jet printing ("IJP"). IJP is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for dyes and inks used in IJP. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle.

WO 01/48090 relates to metal chelate azo compounds which comprise a naphthol component and heterocyclic groups. WO 01/48090 does not disclose such compounds further substituted by a triazole ring.

According to a first aspect of the present invention there is provided a metal chelate compound of the Formula (1) and salts thereof:



Formula (1)

wherein:

one of A and B is OH and the other is an azotriazole group;

each X independently is a substituent other than H, sulphonamido, carboxy, sulpho and carbonamido;

J is a sulphonamido group;

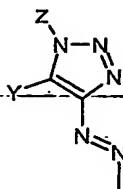
M is a metal or boron;

n and a are each independently 0, 1, 2, 3 or 4;

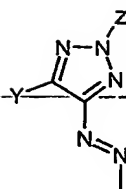
q is 1, 2, 3 or 4; and

(a+q+n) is 1, 2, 3 or 4.

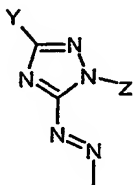
Preferred azotriazole groups are of the Formula (2a), (2b), (2c), (2d) or (2e):



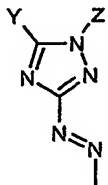
Formula (2a)



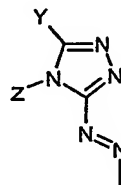
Formula (2b)



Formula (2c)



Formula (2d)



Formula (2e)

wherein:

Z is H, -OH, -Br, -Cl, -F, -CN, -NO<sub>2</sub>, -PO<sub>3</sub>H<sub>2</sub>, -SO<sub>3</sub>H, -CO<sub>2</sub>H, optionally substituted phosphoramidate, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted aralkyl, -SR<sup>1</sup>, -SO<sub>2</sub>R<sup>1</sup>, -SO<sub>2</sub>NR<sup>2</sup>R<sup>3</sup>, -SOR<sup>1</sup>, -OR<sup>1</sup>, -C(O)R<sup>1</sup>, -C(O)OR<sup>1</sup>, -C(O)NR<sup>2</sup>R<sup>3</sup>, -NR<sup>2</sup>R<sup>3</sup>, -NHCOR<sup>1</sup>; and

Y is CF<sub>3</sub> or any one of the groups defined for Z; and

wherein:

R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are each independently H, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl or optionally substituted aralkyl; or

R<sup>2</sup> and R<sup>3</sup> together with the nitrogen to which they are attached form an optionally substituted 5- or 6- membered ring.

When Y or Z is optionally substituted phosphoramidate the phosphoramidate is preferably substituted by optionally substituted alkyl, optionally substituted aryl or optionally substituted aralkyl. Preferred substituents include for example methyl, ethyl, n-propyl, iso-propyl, hydroxyethyl, optionally substituted phenyl or optionally substituted benzyl.

When Y or Z is optionally substituted alkyl, the alkyl group is preferably optionally substituted C<sub>1-4</sub>-alkyl, more preferably C<sub>1-4</sub>-alkyl optionally substituted by halo, hydroxy, carboxy, sulphonyl or cyano. Examples include methyl, ethyl, n-propyl, iso-propyl, trifluoromethyl, hydroxyethyl, cyanoethyl, sulphonylpropyl and carboxyethyl. However, when Y or Z is optionally substituted alkyl it is especially preferred that the alkyl group is methyl, ethyl or trifluoromethyl.

When Y or Z is optionally substituted alkenyl, Y or Z is preferably optionally substituted C<sub>2</sub>-C<sub>4</sub> alkenyl.

When Y or Z is optionally substituted alkynyl, Y or Z is preferably optionally substituted C<sub>2</sub>-C<sub>6</sub> alkynyl.

When Y or Z is optionally substituted aryl the aryl group is preferably optionally substituted phenyl, optionally substituted naphthyl or optionally substituted heteroaryl. It is especially preferred that when Y is optionally substituted aryl it is optionally substituted phenyl or optionally substituted heteroaryl.

Preferred optional substituents on Y when Y is optionally substituted aryl include sulpho, carboxy, nitro, cyano, halo (preferably chloro), alkoxy (preferably C<sub>1-6</sub>-alkoxy), alkyl ((preferably C<sub>1-6</sub>-alkyl) optionally substituted by halogen (preferably fluoro), hydroxy, carboxy, phosphoric acid and sulpho. Especially preferred optional substituents on Y when Y is optionally substituted aryl are selected from C<sub>1-4</sub>-alkyl, carboxy, phosphoric acid and sulpho. However, it is most preferred that when Y is optionally substituted aryl that the aryl group is substituted by carboxy.

Preferred optional substituents on Z when Z is optionally substituted aryl include sulpho, carboxy, nitro, cyano, halo (preferably chloro), alkoxy (preferably C<sub>1-6</sub>-alkoxy), alkyl (preferably C<sub>1-6</sub>-alkyl) optionally substituted by halogen (preferably fluoro), hydroxy, carboxy, phosphoric acid and sulpho. Especially preferred optional substituents on Z as optionally substituted aryl are selected from carboxy or halogen (preferably chloro).

When Y or Z is optionally substituted aralkyl the aralkyl group is preferably optionally substituted benzyl.

However, Y in Formulae (2a), (2b), (2c), (2d) or (2e) is most preferably H, thiol, carboxy, halo (preferably chloro), alkyl ((preferably C<sub>1-6</sub>-alkyl) optionally substituted by hydroxy, carboxy, halo (preferably fluoro) or sulpho. It is especially preferred that Y in Formulae (2a) to (2e) is H, C<sub>1-4</sub>-alkyl or carboxy or sulpho. However, it is most especially preferred that Y is H or CO<sub>2</sub>H.

Z in Formulae (2a) to (2e) is preferably H, ethylester or alkyl (preferably C<sub>1-4</sub>-alkyl) optionally substituted by hydroxy, carboxy, halo (preferably fluoro) or sulpho. It is especially preferred that Z in Formulae (2a) to (2e) is H or C<sub>1-4</sub>-alkyl. However, it is most especially preferred that Z is H.

In one embodiment Z is H and Y is H or CO<sub>2</sub>H.

R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are each independently preferably H, optionally substituted C<sub>1-4</sub>-alkyl or optionally substituted aryl, more preferably H, C<sub>1-4</sub>-alkyl optionally substituted by hydroxy, carboxy, sulpho or cyano or phenyl optionally substituted by hydroxy, carboxy, sulpho, nitro, trifluoromethyl or cyano. Examples of groups represented by R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> include methyl, ethyl, n-propyl, iso-propyl, hydroxyethyl, cyanoethyl, sulphopropyl, carboxyethyl or carboxyphenyl. It is especially preferred however that R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are H, optionally substituted C<sub>1-4</sub>-alkyl for example, trifluoromethyl, hydroxyethyl or cyanoethyl, or optionally substituted aryl for example phenyl optionally substituted by

carboxy; or  $R^2$  and  $R^3$  together with the nitrogen to which they are attached form a 5- or 6-membered ring (preferably morpholine, piperidine or piperazine).

The optional substituent X is preferably -OH, -Br, -Cl, -F, -CF<sub>3</sub>, -CN, -NO<sub>2</sub>, -PO<sub>3</sub>H<sub>2</sub>, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted aralkyl, -SR<sup>1</sup>, -SO<sub>2</sub>R<sup>1</sup>, -SOR<sup>1</sup>, -OR<sup>1</sup>, -C(O)R<sup>1</sup>, -C(O)OR<sup>5</sup>, or -NR<sup>3</sup>R<sup>4</sup>;

wherein:

$R^1$ ,  $R^3$  and  $R^4$  are each independently H, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl or optionally substituted aralkyl; or

$R^3$  and  $R^4$  together with the nitrogen to which they are attached form an optionally substituted 5 or 6 membered ring;

and  $R^5$  is any one of the groups defined for  $R^1$  other than H.

When X is optionally substituted alkyl it is preferably optionally substituted C<sub>1-4</sub>-alkyl, more preferably C<sub>1-4</sub>-alkyl optionally substituted by halogen, hydroxy, carboxy, sulpho or cyano. Examples include ethyl, n-propyl, iso-propyl, hydroxyethyl, cyanoethyl, sulpho, propyl and carboxyethyl. However, when X is optionally substituted C<sub>1-4</sub>-alkyl it is especially preferred that it is substituted by cyano or halogen (preferably fluoro).

When X is optionally substituted alkenyl, it is preferably optionally substituted C<sub>2</sub>-C<sub>4</sub> alkenyl.

When X is optionally substituted alkynyl, it is preferably optionally substituted C<sub>2</sub>-C<sub>6</sub> alkynyl.

When X is optionally substituted aryl it is preferably optionally substituted phenyl or optionally substituted naphthyl. It is especially preferred that when Y is optionally substituted aryl it is optionally substituted phenyl.

Preferred optional substituents on X when X is optionally substituted aryl include: sulpho, carboxy, halogen (preferably chloro) alkoxy (preferably C<sub>1-6</sub>-alkoxy) or alkyl (preferably C<sub>1-6</sub>-alkyl) optionally substituted by halogen, nitro, cyano, hydroxy, carboxy, phosphoric acid or sulpho.

When X is optionally substituted aralkyl it is preferably optionally substituted by benzyl.

It is especially preferred that X is an electron withdrawing group for example nitro, cyano or trifluoromethyl.

It is most especially preferred that X is CN.

J is preferably of the Formula SO<sub>2</sub>NR<sup>6</sup>R<sup>7</sup>, wherein  $R^6$  and  $R^7$  are each independently H, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted aralkyl; or

$R^6$  and  $R^7$  together with the nitrogen to which they are attached form an optionally substituted 5- or 6- membered ring.



When  $R^6$  or  $R^7$  is optionally substituted alkyl each is preferably optionally substituted  $C_{1-4}$ -alkyl, more preferably  $C_{1-4}$ -alkyl optionally substituted by halogen, hydroxy, carboxy, sulpho or cyano. Examples include ethyl, n-propyl, iso-propyl, hydroxyethyl, cyanoethyl, sulpho, propyl and carboxyethyl. However, when either of  $R^{10}$  and  $R^{11}$  is optionally substituted  $C_{1-4}$ -alkyl it is especially preferred that each is substituted by cyano or halogen (preferably fluoro).

When  $R^6$  or  $R^7$  is optionally substituted alkenyl, each is preferably optionally substituted  $C_2-C_4$  alkenyl.

When  $R^6$  or  $R^7$  is optionally substituted alkynyl, each is preferably optionally substituted  $C_2-C_6$  alkynyl.

When  $R^6$  or  $R^7$  is optionally substituted aryl each is preferably optionally substituted phenyl or optionally substituted naphthyl. It is especially preferred that when  $R^6$  or  $R^7$  is optionally substituted aryl each is optionally substituted phenyl.

Preferred optional substituents on  $R^6$  or  $R^7$  when  $R^6$  or  $R^7$  is optionally substituted aryl include: sulpho, carboxy, nitro, cyano, halogen (preferably chloro) alkoxy (preferably  $C_{1-6}$ -alkoxy) or alkyl (preferably  $C_{1-6}$ -alkyl) optionally substituted by halogen, (preferably fluoro), hydroxy, carboxy, phosphoric acid or sulpho.

When  $R^6$  or  $R^7$  is optionally substituted aralkyl each is preferably optionally substituted by benzyl.

$R^6$  and  $R^7$  are each most preferably independently H, or optionally substituted aryl, most preferably optionally substituted phenyl or optionally substituted naphthyl. Especially preferred optional substituents on  $R^6$  or  $R^7$  when  $R^6$  or  $R^7$  are optionally substituted aryl include  $C_{1-4}$ -alkyl, carboxy, phosphoric acid or sulpho. However, it is most especially preferred that  $R^6$  or  $R^7$  are independently H or optionally substituted aryl with the aryl group substituted by a carboxylic group.

M preferably comprises boron or one or more of the following metals: nickel, chromium, cobalt, copper, zinc, iron or manganese. However, it is particularly preferred that M is nickel. M is preferably able to co-ordinate to the portion of the compound of Formula (1) in square brackets in the ratio 1:1, 2:1, 2:2, 2:3 respectively. However, it is also preferred that M is able to co-ordinate to the portion of the compound in of Formula (1) in square brackets in the ratio 1:1 and 2:1.

It is preferable that n is 0, 1 or 2, more preferably 1 or 2 and especially 1.

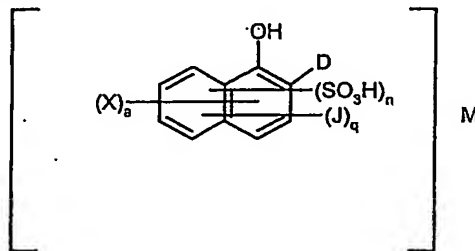
It is preferred that a is 0, 1, 2 or 3, more preferably 0, 1 or 2 and especially 0 or 1. Most especially it is preferred that a is 0.

It is preferred that q is 1 or 2.

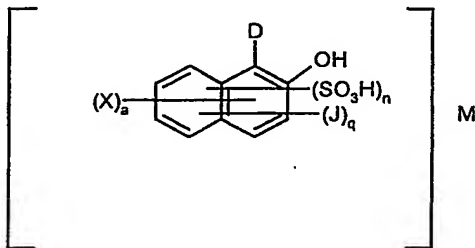
Preferably the value of (a+q+n) is 2 or 3.

Preferably the compound of Formula (1) comprises one or more water-solubilising groups, for example such as sulpho, carboxy or phosphoric acid groups.

It is especially preferred that the compound of Formula (1) is a metal chelate compound of the Formula (3) or (4):



Formula (3)



Formula (4)

wherein:

D is an azotriazole group, preferably of the Formula (2a), (2b), (2c), (2d) or (2e) as hereinbefore defined;

q is 1 or 2;

n is 1 or 2;

a is 0 or 1;

M is a metal, preferably nickel; and

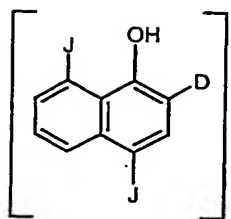
J and X are as hereinbefore defined.

Preferably (a+q+n) is 2 or 3.

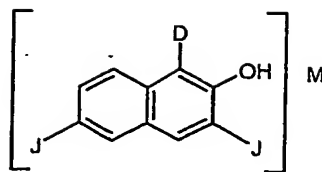
When the metal chelate compound is of Formula (3), it is preferred that there is one sulphonamido group at the 4-position on the naphthylene ring and one sulphonamido group at the 8-position on the naphthylene ring, relative to D being at the 2-position on the naphthylene ring.

When the metal chelate compound is of Formula (4), it is preferred that there is at least one sulphonamido group at the 3-position on the naphthylene ring or one sulphonamido group at the 6-position on the naphthylene ring, relative to D being at the 1-position on the naphthylene ring.

In view of the foregoing preferences the compound of Formula (1) is preferably a metal chelate compound of the Formula (5) or (6) or a salt thereof:



Formula (5)



Formula (6)

wherein:

D, M and J are as hereinbefore defined in relation to Formula (1).

In Formula (5) and (6) D is preferably of Formulae (2a), (2b), (2c), (2d) or (2e) as hereinbefore defined.

It is especially preferred that for the compound of Formula (5) or (6) J is  $\text{SO}_2\text{NR}^6\text{R}^7$  wherein one of  $\text{R}^6$  or  $\text{R}^7$  is H and the other is optionally substituted aryl, more especially an aryl group carrying a carboxy group. However, it is most preferred that one of  $\text{R}^6$  or  $\text{R}^7$  is H and the other is a carboxy phenyl group.

It is especially preferred that the compound of Formula (1) is magenta in colour.

The compounds of Formula (1) provide prints which exhibit a high light-fastness and good optical density when incorporated into inks for ink jet printing. The compounds of Formula (1) are also highly soluble which improves operability and reduces crusting and nozzle blockage when inks containing the compounds are used in an ink jet printer.

Compounds of the present invention Formula (1) are preferably free from fibre reactive groups. The term fibre reactive group is well known in the art and is described for example in EP 0356014 A1. Fibre reactive groups are capable, under suitable conditions, of reacting with the hydroxyl groups present in cellulosic fibres or with the amino groups present in natural fibres to form a covalent linkage between the fibre and the dye. As examples of fibre reactive groups preferably not present in the compounds of Formula (1) there may be mentioned aliphatic sulphonyl groups which contain a sulphate ester group in beta-position to the sulphur atom, e.g. beta-sulphato-ethylsulphonyl groups, alpha, beta-unsaturated acyl radicals of aliphatic carboxylic acids, for example acrylic acid, alpha-chloro-acrylic acid, alpha-bromoacrylic acid, propiolic acid, maleic acid and mono- and dichloro maleic; also the acyl radicals of acids which contain a substituent which reacts with cellulose in the presence of an alkali, e.g. the radical of a halogenated aliphatic acid such as chloroacetic acid, beta-chloro and beta-bromopropionic acids and alpha, beta-dichloro- and dibromopropionic acids or radicals of vinylsulphonyl- or beta-chloroethylsulphonyl- or beta-sulphatoethyl-sulphonyl-endo- methylene cyclohexane carboxylic acids. Other examples of cellulose reactive groups are tetrafluorocyclobutyl carbonyl, trifluoro-cyclobutenyl carbonyl, tetrafluorocyclobutylethenyl carbonyl, trifluoro-cyclobutenylethenyl-carbonyl; activated-halogenated-1,3-dicyanobenzene-radicals; and

heterocyclic radicals which contain 1, 2 or 3 nitrogen atoms in the heterocyclic ring and at least one cellulose reactive substituent on a carbon atom of the ring.

The compounds of the invention may be in the free acid or salt form. Preferred salts are water-soluble, for example alkali metal salts, especially lithium, sodium, potassium, ammonium, substituted ammonium and mixed salts thereof. Preferred alkali metal salts are those with sodium, lithium, ammonium and substituted alkyl ammonium salts.

Preferred ammonium and substituted ammonium salts have cations of the formula  $^+NV_4$  wherein each V independently is H or optionally substituted alkyl, or two groups represented by V are H or optionally substituted alkyl and the remaining two groups represented by V, together with the N atom to which they are attached, form a 5- or 6-membered ring (preferably a morpholinyl, pyridinyl or piperidinyl ring).

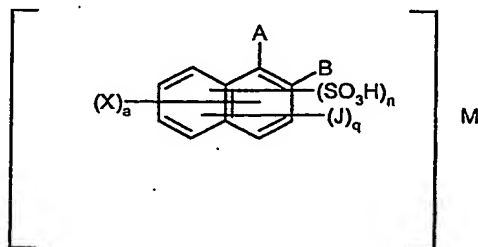
Preferably each V independently is H or  $C_{1-4}$ -alkyl, more preferably H,  $CH_3$  or  $CH_3CH_2$ , especially H.

Examples of cations include  $^+NH_4$ , morpholinium, piperidinium, pyridinium,  $(CH_3)_3N^+H$ ,  $(CH_3)_2N^+H_2$ ,  $H_2N^+(CH_3)(CH_2CH_3)$ ,  $CH_3N^+H_3$ ,  $CH_3CH_2N^+H_3$ ,  $H_2N^+(CH_2CH_3)_2$ ,  $CH_3CH_2CH_2N^+H_3$ ,  $(CH_3)_2CHN^+H_3$ ,  $N^+(CH_3)_4$ ,  $N^+(CH_2CH_3)_4$ , N-methyl pyridinium, N,N-dimethyl piperidinium and N,N-dimethyl morpholinium.

It is especially preferred that the compound is in the form of a sodium, lithium, potassium, ammonium or substituted ammonium salt because we have found that these salts provide prints which exhibit a high light-fastness when incorporated into an ink jet printing ink.

The compounds of Formula (1) may be converted into a salt using known techniques. For example, an alkali metal salt of a compound may be converted into a salt with ammonia or an amine by dissolving an alkali metal salt of the dye in water, and passing the solution through a column of a suitably modified ion exchange resin.

The compounds of the invention may be prepared using conventional techniques for the preparation of metal chelate compounds. For example a suitable method comprises adding together a solution of a metal salt to a solution of a compound of Formula (7):



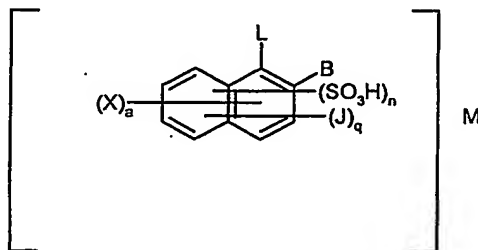
Formula (7)

wherein;

A, B, J, n, a and q are as hereinbefore defined.

The product of the above process may be converted to a salt by conventional techniques as hereinbefore described. Alternatively the product may be isolated in its free acid form by acidifying the reaction mixture, preferably using a mineral acid, for example hydrochloric acid and when the product precipitates as a solid it may be separated from the mixture by filtration. Unwanted anions may be and preferably are removed from the product of the process by dialysis, osmosis, ultrafiltration or a combination thereof. Alternatively, the product solution is subjected to the above purification directly without isolation of the product.

The compounds of Formula (7) may be prepared, for example, by by diazotising a compound of the formula  $A^1-NH_2$  to give a diazonium salt and coupling the resultant diazonium salt with a compound of the Formula (7a):



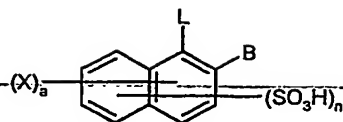
Formula (7a)

wherein  $A^1$  is a triazole group, one of L or B is OH and the other is H, and X, J, a, n and q are as hereinbefore defined in relation to Formula (1).

The diazotisation is preferably performed at a temperature below  $6^\circ C$ , more preferably at a temperature in the range  $-10^\circ C$  to  $5^\circ C$ . Preferably the diazotisation is performed in water, preferably at a pH below 7. Dilute mineral acid, e.g. HCl or  $H_2SO_4$ , are often used to achieve the desired acidic conditions.

The compound of Formula (7a) may be prepared for example by:

- (i) reacting a compound of the formula (7b) with acetic anhydride to protect the OH group by forming an acetyl group;
- (ii) reacting the product from stage (i) with phosphorous oxychloride to convert at least some of the sulphonic acid groups to sulfonyl chloride groups;
- (iii) condensing the product of stage (ii) with an amine; and
- (iv) removing of the acetyl protecting group with sodium hydroxide solution;



Formula (7b)

wherein L, B, X, a and n are as hereinbefore defined.

The present invention also covers mixtures comprising two or more compounds of the Formula (1) or salts thereof. Furthermore, the compounds of Formula (1) may be mixed with commercially available dyes, especially those listed in the International Colour Index, to adjust the shade or other properties as desired.

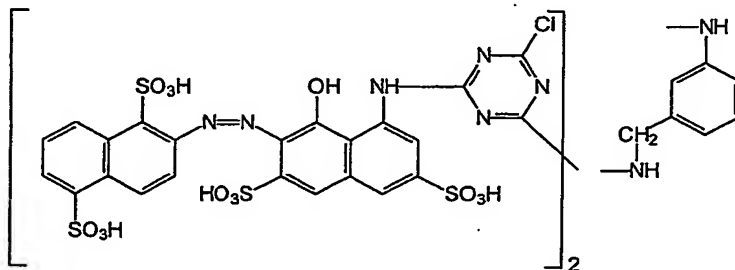
According to a second aspect of the present invention there is provided a composition comprising:

- (a) one or more compound according to the first aspect of the present invention; and
- (b) one or more water-soluble dye other than a compound according to the first aspect of the invention.

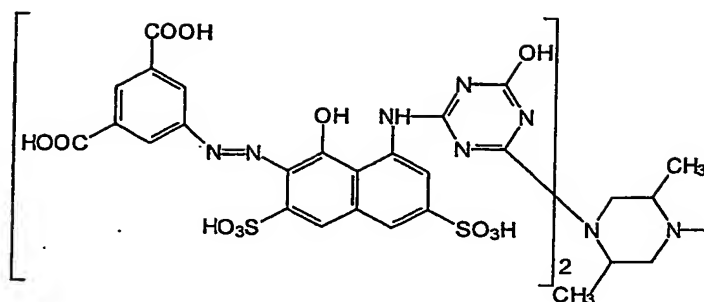
The water-soluble dye is preferably a water-soluble magenta dye, for example, a xanthene dye, an azo or bis azo dye, more preferably an anionic azo or bis azo dye and especially an azo or bis azo dye which contains one or more groups selected from sulphonate, carboxylate and thiocarboxylate groups.

Preferred water-soluble magenta dyes include C.I. Acid Red 50, 52, 87, 91, 92, 95, 249 and 289; C.I. Direct Violet 106 and 107; compounds 100 to 107, 200 and 201 described on pages 8 and 9 of WO96/24636; compounds 1 to 24 shown described on columns 4 to 10 in US 5,542,970; compounds 1 to 55 described on pages 7 to 17 of EP-A-682 088; compounds 1 to 14 shown in Example 1 to 6 of EP-A-194,885; compounds 1 to 24 described on pages 8 to 13 of EP-A-717 089; the compounds described in examples 1 to 16 in columns 5 to 11 of US 5,262,527; and the dyes described in Examples 1 to 21 in WO 94/16021.

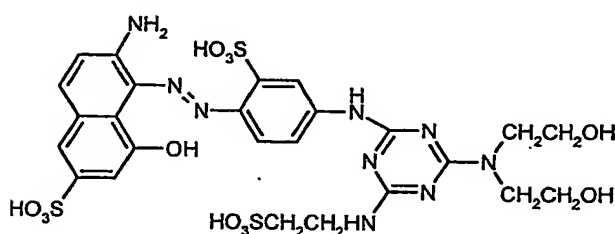
Especially preferred water-soluble magenta dyes for use in the composition according to the second aspect of the invention include C.I. Acid Red 52, C.I. Acid Red 289 or a dye of the Formula (8), (9) and (10) and salts thereof:



Formula (8)



Formula (9)



Formula (10)

The dye of Formula (8) may be prepared using the method described in Example 1 of EP 0 559 310. The dye of the Formula (9) may be prepared using the method described in Example 3 of PCT publication number WO 94/16021. The dye of Formula (10) may be prepared using the method described in Example 1 of WO 96/24636.

The composition according to the second aspect of the present invention preferably comprises:

- (a) from 1 to 99, more preferably from 3 to 70 and especially from 5 to 50 parts in total of the compound(s) according to the first aspect of the invention; and
- (b) from 99 to 1, more preferably from 30 to 97 parts and especially 95 to 50 parts in total of the water-soluble magenta dye(s);

wherein the parts are by weight and the sum of the parts (a) + (b) = 100.

The composition may contain a single dye of Formula (1) or a mixture thereof. Similarly, the composition may contain a single water-soluble magenta dye or a mixture of two or more water-soluble magenta dyes.

The compounds and compositions according to the first and second aspects of the present invention may be, and preferably are, purified to remove undesirable impurities before they are incorporated into inks for ink jet printing. Conventional techniques may be employed for purification, for example ultrafiltration, reverse osmosis and/or dialysis.

According to a third aspect of the present invention there is provided an ink comprising:

- (a) a compound according to the first aspect of the present invention, or a composition according to the second aspect of the invention; and

(b) a liquid medium.

... Preferably component (a) of the ink is or comprises one of the preferred  
compounds or compositions as hereinbefore described in relation to the first or second aspect of the invention.

The liquid medium preferably comprises:

- (i) water;
- (ii) a mixture of water and an organic solvent; or
- (iii) an organic solvent free from water.

The number of parts by weight of component (a) of the ink is preferably from 0.01 to 30, more preferably 0.1 to 20, especially from 0.5 to 15, and more especially from 1 to 5 parts. The number of parts by weight of component (b) is preferably from 99.99 to 70, more preferably from 99.9 to 80, especially from 99.5 to 85, and more especially from 99 to 95 parts. The number of parts (a) + (b) is 100 and all parts mentioned herein are by weight.

Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of concentrates which may be used to prepare more dilute inks and reduces the chance of the compound(s) of component (a) of the ink precipitating if evaporation of the liquid medium occurs during storage.

When the liquid medium comprises a mixture of water and an organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C<sub>1-6</sub>-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C<sub>1-4</sub>-alkyl ethers of diols, preferably mono-C<sub>1-4</sub>-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy) ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulfoxides, preferably dimethyl sulfoxide and



sulpholane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-miscible organic solvents.

Especially preferred water-soluble organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C<sub>1-4</sub>-alkyl and C<sub>1-4</sub>-alkyl ethers of diols, more preferably mono- C<sub>1-4</sub>-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

A preferred liquid medium comprises:

- (a) from 75 to 95 parts water; and
- (b) from 25 to 5 parts in total of one or more solvents selected from diethylene glycol, 2-pyrrolidone, thiodiglycol, N-methylpyrrolidone, cyclohexanol, caprolactone, caprolactam and pentane-1,5-diol;

wherein the parts are by weight and the sum of the parts (a) and (b) = 100.

Another preferred liquid medium comprises:

- (a) from 60 to 80 parts water;
- (b) from 2 to 20 parts diethylene glycol; and
- (c) from 0.5 to 20 parts in total of one or more solvents selected from 2-pyrrolidone, N-methylpyrrolidone, cyclohexanol, caprolactone, caprolactam, pentane-1,5-diol and thiodiglycol;

wherein the parts are by weight and the sum of the parts (a), (b) and (c) = 100.

Examples of further suitable ink media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore defined water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH<sub>2</sub>Cl<sub>2</sub>; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the dye in the liquid medium. Examples of polar solvents include C<sub>1-4</sub>-alcohols. In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) and/or an alcohol (especially a C<sub>1-4</sub>-alkanol, such as ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected which gives good control over the drying characteristics and storage stability of the ink.

Ink media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

An especially preferred ink comprises:

- (a) from 1 to 10 parts in total of a compound or composition according to the first or second aspect of the invention;
- (b) from 2 to 60, more preferably 5 to 40 parts of water-soluble organic solvent; and
- (c) from 30 to 97, more preferably 40 to 85 parts water;

wherein all parts are by weight and the sum of the parts (a) + (b) + (c) = 100.

When the liquid medium in the ink comprises a mixture of water and an organic solvent; or an organic solvent free from water, component (a) of the ink may comprise a compound of the Formula (1) as hereinbefore defined in relation to the first aspect of the invention.

Preferred low melting solid media have a melting point in the range from 60°C to 125°C. Suitable low melting point solids include long chain fatty acids or alcohols, preferably those with C<sub>18-24</sub> chains, and sulphonamides. The dye of Formula (1) may be dissolved in the low melting point solid or may be finely dispersed in it.

The inks according to the present invention may also contain additional components conventionally used in ink jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, fogging reducing additives, anti-cockle agents to reduce paper curling and surfactants which may be ionic or non-ionic.

The pH of the ink is preferably from 4 to 11, more preferably from 7 to 10.

The viscosity of the ink at 25°C is preferably less than 50cP, more preferably less than 20 cP and especially less than 5cP.

When the inks according to the invention are used as ink jet printing inks, the ink preferably has a concentration of less than 500 parts per million, more preferably less than 100 parts per million of halide ions. It is especially preferred that the ink has less than 100, more preferably less than 50 parts per million of divalent and trivalent metals, wherein parts refer to parts by weight relative to the total weight of the ink. We have found that purifying the inks to reduce the concentration of these undesirable ions reduces nozzle blockage in ink jet printing heads, particularly in thermal ink jet printers.

A fourth aspect of the present invention provides a process for printing an image on a substrate comprising applying thereto by means of an ink jet printer an ink containing a

compound according to the first aspect of the invention or a composition according to the second aspect of the invention.

The ink used in this process is preferably as defined in the third aspect of the present invention.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the orifice.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Examples of commercially available papers include, HP Premium Coated Paper, HP Photopaper (all available from Hewlett Packard Inc.), Stylus Pro 720 dpi Coated Paper, Epson Photo Quality Glossy Film, Epson Photo Quality Glossy Paper (available from Seiko Epson Corp.), Canon HR 101 High Resolution Paper, Canon GP 201 Glossy Paper, Canon HG 101 High Gloss Film (all available from Canon Inc.), Wiggins Conqueror paper (available from Wiggins Teape Ltd), Xerox Acid Paper and Xerox Alkaline paper, Xerox Acid Paper (available from Xerox).

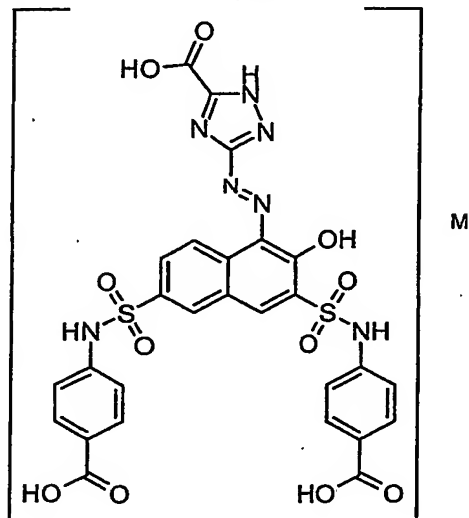
A fifth aspect of the present invention provides a substrate, preferably a paper, an overhead projector slide or a textile material, printed with an ink according to the third aspect of the present invention or by means of the process according to the fourth aspect of the present invention.

According to a sixth aspect of the present invention there is provided an ink jet printer cartridge comprising a chamber and ink, wherein the ink is present in the chamber and the ink contains a compound or a composition according to the first or second aspect of the present invention. Preferably the ink is an ink according to the third aspect of the present invention.

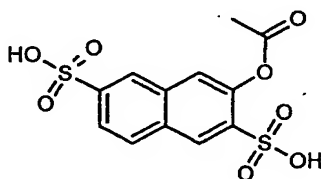
According to a seventh aspect of the present invention there is provided an ink jet printer containing an ink jet printer cartridge, wherein the ink jet printer cartridge is as defined in the sixth aspect of the present invention.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

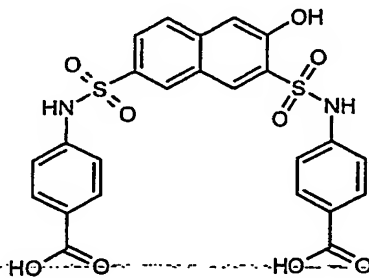
The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

Example 1Preparation of Compound (1) wherein M is nickel

Compound (1)

Stage (a): Preparation of 2-acetoxynaphthalene-3,6-disulphonic acid.

Acetic anhydride (350 ml, 3.8mol) was added dropwise to a suspension of 2-hydroxynaphthalene-3,6-disulphonic acid di sodium salt (87g, 0.25mol) in *N,N*-dimethylacetamide (350ml). The reaction mixture was stirred at 125°C for 24 hours, cooled to room temperature and added to acetone (2500ml). The product was filtered off, washed with acetone (3 x 100ml) and dried to give 95.2g of a cream coloured solid.

Stage (b): Preparation of 3,6-bis-(4-carboxy-phenylsulfamoyl)-2-hydroxy-naphthalene

$\text{POCl}_3$  (50ml, 0.538mol) was added dropwise to a suspension of the product from stage (a) (50g, 0.128mol) in acetonitrile (250ml) at reflux. The reaction mixture was stirred for 3 hours at  $70^\circ\text{C}$ , cooled, added to ice / water (4000ml) and the naphthalene disulfonyl chloride extracted with dichloromethane (4 x 300ml). The combined extracts were dried with  $\text{MgSO}_4$ , evaporated under reduced pressure and the residue dissolved in N,N-dimethylacetamide (400 ml). 4-Aminobenzoic acid (34.3g, 0.25mol) was added to the above solution, the reaction mixture was stirred overnight at room temperature and then added to water (3000ml). The pH was then lowered to 0.5 with concentrated  $\text{H}_2\text{SO}_4$  and the precipitated product extracted from ethyl acetate (4 x 300ml). The combined extracts were washed with 1N HCl (600ml), dried with  $\text{MgSO}_4$  and evaporated under reduced pressure. The residue was dissolved in water (1000ml) at pH 12 (2N NaOH) and then stirred for 1 hour at  $50-60^\circ\text{C}$ . The solution was allowed to cool, the pH lowered to pH 4 with concentrated HCl and the product filtered off and dried to give 41.5g (53% yield) of a tan coloured solid.

#### Stage (c):

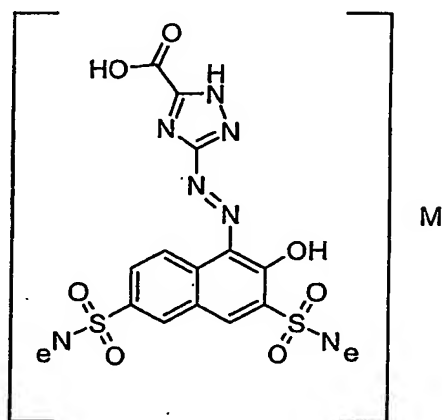
3-amino-1,2,4-triazole-5-carboxylic acid hydrate (1.28g, 0.01mol) was suspended in water (50ml) and dissolved by the addition of 2M NaOH to pH 8. Sodium nitrite (0.76g, 0.011mol) was added and the solution stirred until the sodium nitrite had dissolved. The mixture was then added dropwise to a cooled mix of ice-water (30g) and concentrated HCl (3.0ml) at  $0-5^\circ\text{C}$ , the mixture was stirred for 30 minutes. at  $0-5^\circ\text{C}$  and then excess nitrous acid was removed by adding sulphamic acid. The diazo suspension was added slowly to a solution of the product from stage (b) (5.42g, 0.01mol) in water (100ml) at pH 7-8 (2N NaOH) cooled below  $5^\circ\text{C}$ . The reaction mixture was then stirred at  $0-5^\circ\text{C}$  for one further hour, the product was precipitated by acidification to pH 4 with 2N HCl and collected by filtration. The product was then washed with water and dried in a vacuum desiccator to give 6.4g of an orange solid.

#### Stage (d): Preparation of Compound (1).

A solution of nickel acetate tetrahydrate (1.38g, 0.0055mol) in water (10ml) was added dropwise to the product from stage (c) (5.0g, 0.0073mol) dissolved in water (100ml) at pH 7 (2N NaOH). The reaction mixture was stirred for 2 hours at ambient temperature, dialysed using SpectraPor membrane tubing (molecular weight cut off 3500) to low conductivity ( $<100\mu\text{S}$ ). The product was obtained by evaporation under reduced pressure to afford a dark crystalline solid (6g). Analysis by mass spectrometry found  $m/z$  1419. Requires  $M^+ = 1420$ .

Examples 2 to 5

Compounds (2) to (5) described in Table 1 of the Formula (11) were prepared using an analogous process to that described in Example 1 except that in stage (b) the amino compound shown in Table 1 was used in place of 4-aminobenzoic acid.



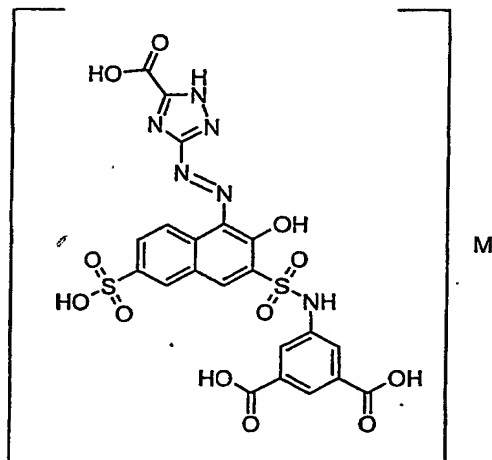
Formula (11)

Table 1

Example	Amino compound (N <sub>e</sub> -H)	Mass Spectra Analysis	Compound
2		m/z 824 (M-H) <sup>-</sup>	(2)
3		m/z 147 (M-H) <sup>-</sup>	(3)
4		Not measured	(4)
5		m/z 720 (M-H) <sup>-</sup>	(5)

Example 6

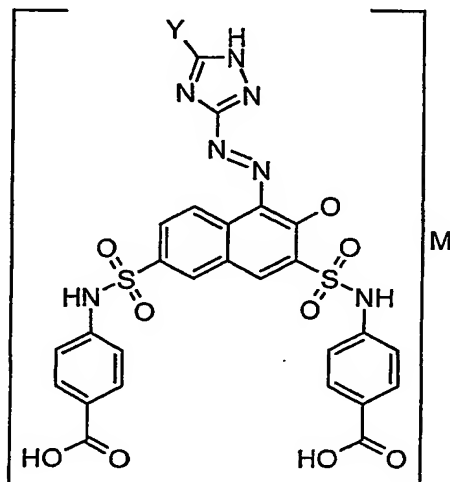
Compound (6) was prepared using an analogous process to that described in Example 1 except that in stage (b) 5-aminoisophthalic acid was used in place of 4-aminobenzoic acid in a 1:1 molar ratio (5-aminoisophthalic acid : disulfonyl chloride).



Compound (6)

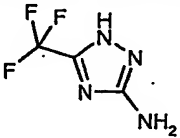
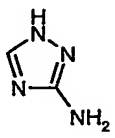
Examples 7 and 8

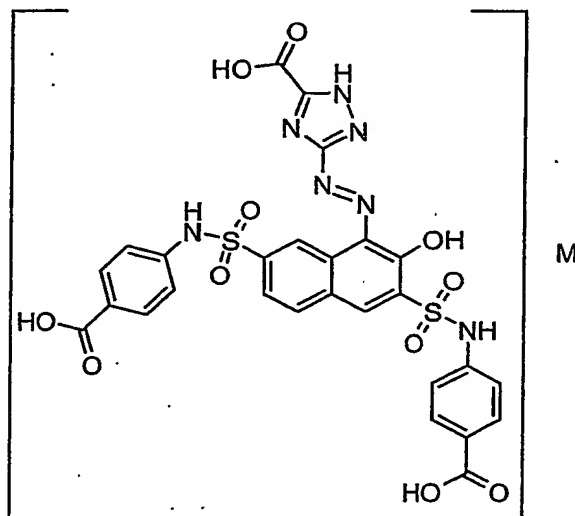
Compounds (7) and (8) described in Table 2 of the Formula (12) were prepared using an analogous process to that described in Example 1 except that in stage (c) the amino triazole compound shown in Table 2 was used in place of 3-amino-1,2,4-triazole-5-carboxylic acid.



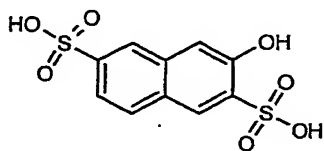
Formula (12)

Table 2

Example	Amino Triazole	Dye name
7		Nickel chelate of 5-[3,6-bis-(4-carboxy-phenylsulfamoyl)-2-hydroxy-naphthalen-1-ylazo]-4H-[1,2,4]triazole-3-trifluoromethyl. ("Compound (7)"). Analysis by mass spectrometry found $m/z$ 1465 (M-H) <sup>-</sup> .
8		Nickel chelate of 5-[3,6-bis-(4-carboxy-phenylsulfamoyl)-2-hydroxy-naphthalen-1-ylazo]-4H-[1,2,4]triazole. ("Compound (8)"). Analysis by mass spectrometry found $m/z$ 1329 (M-H) <sup>-</sup> .

Example 9Preparation of Compound (9) wherein M is nickel

Compound (9)

Stage (a): Preparation of 3-hydroxynaphthalene-2,6-disulfonic acid.



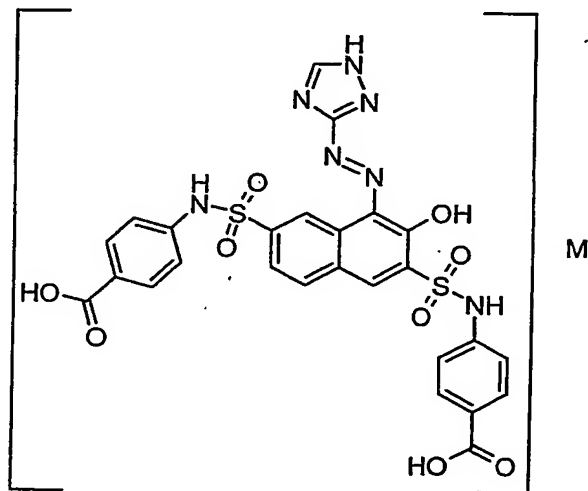
7-Hydroxynaphthalene-2-sulfonic acid (250g, 1.16mol) was added in portions to a mixture of concentrated  $\text{H}_2\text{SO}_4$  (950g) and water (50g). The mixture was stirred at 110 – 120°C for 3 hours, cooled to room temperature, added to a mixture of ice and water (5000ml) and the product precipitated by the addition of sodium chloride. The slurry was warmed to 90°C to dissolve the product, stirred for 1 hour at this temperature and then allowed to cool. The product was filtered off and the damp product dissolved in water (3000ml) at pH 10 by the addition of concentrated sodium hydroxide solution. The solution was then filtered to remove a small amount of insoluble material. The pH of the filtrate was lowered to 7 with concentrated HCl and the product precipitated by the addition sodium chloride. The product was filtered off and dried in a vacuum oven to give 117g of a cream coloured solid (68% yield).

Stage (b):

Compound (9) was prepared using an analogous process to that described in Example 1 except that in stage (a) 3-hydroxynaphthalene-2,6-disulfonic acid was used in place of 2-hydroxynaphthalene-3,6-disulphonic acid. Analysis by mass spectrometry found  $m/z$  1417 (M-H).

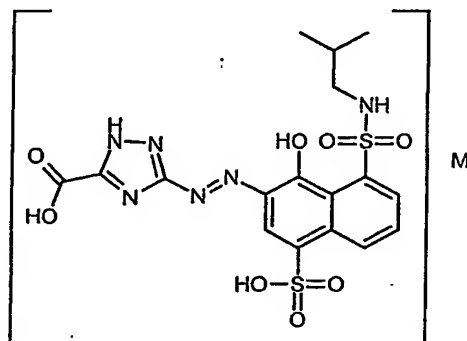
Example 10

Preparation of Compound (10) wherein M is nickel

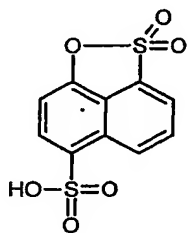


(10):

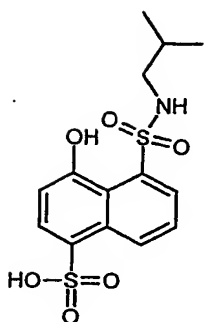
Compound (10) was prepared using an analogous process to that described in Example 1 except that in stage (a) 3-hydroxynaphthalene-2,6-disulfonic acid was used in place of 2-hydroxynaphthalene-3,6-disulphonic acid and in stage (c) 3-amino-1,2,4-triazole was used in place of 3-amino-1,2,4-triazole-5-carboxylic acid.

Example 11Preparation of Compound (11) wherein M is nickel

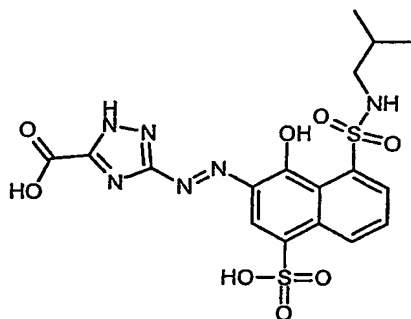
Dye (11)

Stage (a):

1,8-Naphthosultone (25g, 0.119mol) was added in portions to concentrated  $\text{H}_2\text{SO}_4$  (75ml). The mixture was then stirred at  $80^\circ\text{C}$  for 1 hour allowed to cool and then added slowly to ice-water (150ml) maintaining the temperature below  $40^\circ\text{C}$ . Sodium sulphate (46g) was added to the reaction mixture, the resulting suspension was stirred for 10 minutes and then collected by filtration. The damp product was dissolved in water (150ml) by warming to  $45\text{--}50^\circ\text{C}$  and then precipitated by adding sodium chloride (35g) and allowing to cool. The product was collected by filtration and dried in a vacuum oven at  $40^\circ\text{C}$  to give 40g of a cream solid (86% yield).

Stage (b)

The product from stage (a) (10g, 0.035mol) was added in portions to isobutylamine (25ml). The reaction mixture was stirred for 30. minutes at 40-50°C, evaporated under reduced pressure and the residue slurried in acetone (200ml). The product was collected by filtration and dried to give 6g of a pale green powder.

Stage (c)

3-amino-1,2,4-triazole-5-carboxylic acid hydrate (1.28g, 0.01mol) was suspended in water (50ml) and dissolved by the addition of 2M NaOH to pH 8. Sodium nitrite (0.76g, 0.11mol) was added and the solution stirred until the sodium nitrite had dissolved.

The mixture was then added dropwise to a cooled mix of ice-water (30g) and concentrated HCl (3.0ml) at 0-5°C, the mixture was stirred for 30 minutes at 0-5°C and then excess nitrous acid was removed by adding sulphamic acid. The diazo suspension was added slowly to a solution of the product from stage (b) (3.6g, 0.01mol) in water (100ml) at pH 10-10.5 (2N NaOH) cooled below 5 °C. The reaction mixture was then stirred at 0-5°C for 1 hour, the product was precipitated by acidification to pH 4 with 2N HCl and collected by filtration. The product was washed with water and then dried in a vacuum desiccator to give 4.2g of an orange solid.

Stage (d): Preparation of Compound (11).

Compound (11) was prepared using an analogous process to that described in Example 1, stage (d) except that in place of the product from Example 1, stage (c) there

was used the product from Example 11, stage (c). Analysis by mass spectrometry found  $m/z$  1051 (M-H).

### Inks

The inks described in Tables I and II may be prepared wherein the compound described in the first column is the compound made in the above example of the same number. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink jet printing.

The following abbreviations are used in Table I and II:

PG = propylene glycol

DEG = diethylene glycol

NMP = N-methyl pyrrolidone

DMK = dimethylketone

IPA = isopropanol

MEOH = methanol

2P = 2-pyrrolidone

MIBK = methylisobutyl ketone

P12 = propane-1,2-diol

BDL = butane-2,3-diol

CET = cetyl ammonium bromide

PHO =  $\text{Na}_2\text{HPO}_4$  and

TBT = tertiary butanol

TDG = thiodiglycol

TABLE I

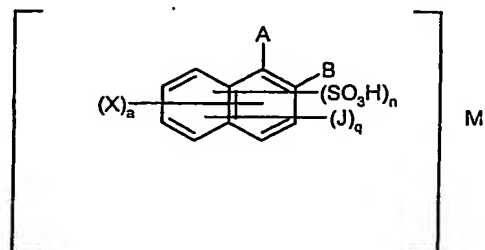
Compound	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	5		0.2			5	1	
3	10.0	85	3		3	3						1
4	2.1	91		8					4			5
5	3.1	86	5				0.5	0.2			9	
6	1.1	81			9			0.5	6	10	5	4
7	2.5	60	4	15	3	3			10			
8	5	65		20								5
9	2.4	75	5	4		5				6		
10	4.1	80	3	5	2	10		0.3				
11	3.2	65		5	4	6			5	4	6	5
11	5.1	96								4		
11	10.8	90	5						5			
2	10.0	80	2	6	2	5			1		4	
3	1.8	80		5							15	
4	2.6	84			11						5	
6	3.3	80	2			10				2		6
5	12.0	90				7	0.3		3			
7	5.4	69	2	20	2	1					3	3
8	6.0	91			4						5	

TABLE II

Compound	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	PI2
1	3.0	80	15			0.2					5	
2	9.0	90		5						1.2		5
3	1.5	85	5	5		0.15	5.0	0.2				
4	2.5	90		6	4					0.12		
5	3.1	82	4	8		0.3						6
6	0.9	85		10					5	0.2		
7	8.0	90		5	5			0.3				
8	4.0	70		10	4				1		4	11
9	2.2	75	4	10	3				2		6	
10	10.0	91			6						3	
11	9.0	76		9	7		3.0			0.95	5	
1	5.0	78	5	11							6	
3	5.4	86			7						7	
7	2.1	70	5	5	5	0.1	0.2	0.1	5	0.1	5	
5	2.0	90		10								
9	2	88						10				
11	5	78			5			12			5	
1	8	70	2		8			15			5	
2	10	80						8			12	
1	10	80		10								

CLAIMS

1. A metal chelate compound of the Formula (1) and salts thereof:



Formula (1)

wherein:

one of A and B is OH and the other is an azotriazole group;

each X independently is a substituent other than H, sulphonamido, carboxy, sulpho and carbonamido;

J is a sulphonamido group;

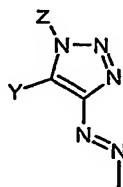
M is a metal or boron;

n and a are each independently 0, 1, 2, 3 or 4;

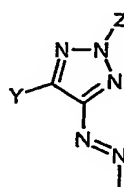
q is 1, 2, 3 or 4; and

(a+q+n) is 1, 2, 3 or 4.

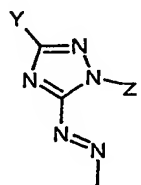
2. A compound according to claim 1 wherein the azotriazole group is of the Formula (2a), (2b), (2c), (2d) or (2e):



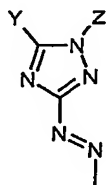
Formula (2a)



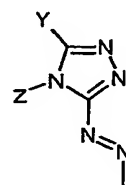
Formula (2b)



Formula (2c)



Formula (2d)



Formula (2e)

wherein:

Z is H, -OH, -Br, -Cl, -F, -CN, -NO<sub>2</sub>, -PO<sub>3</sub>H<sub>2</sub>, -SO<sub>3</sub>H, -CO<sub>2</sub>H, optionally substituted phosphoramidate, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted aralkyl, -SR<sup>1</sup>, -SO<sub>2</sub>R<sup>1</sup>, -SO<sub>2</sub>NR<sup>2</sup>R<sup>3</sup>, -SOR<sup>1</sup>, -OR<sup>1</sup>, -C(O)R<sup>1</sup>, -C(O)OR<sup>1</sup>, -C(O)NR<sup>2</sup>R<sup>3</sup>, -NR<sup>2</sup>R<sup>3</sup>, -NHCOR<sup>1</sup>; and

Y is CF<sub>3</sub> or any one of the groups defined for Z; and

wherein:

R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are each independently H, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl or optionally substituted aralkyl; or

R<sup>2</sup> and R<sup>3</sup> together with the nitrogen to which they are attached form an optionally substituted 5- or 6- membered ring.

3. A compound according to claim 1 or 2 wherein X is -OH, -Br, -Cl, -F, -CF<sub>3</sub>, -CN, -NO<sub>2</sub>, -PO<sub>3</sub>H<sub>2</sub>, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted aralkyl, -SR<sup>1</sup>, -SO<sub>2</sub>R<sup>1</sup>, -SOR<sup>1</sup>, -OR<sup>1</sup>, -C(O)R<sup>1</sup>, -C(O)OR<sup>5</sup>, or -NR<sup>3</sup>R<sup>4</sup>;

wherein:

R<sup>1</sup>, R<sup>3</sup> and R<sup>4</sup> are each independently H, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl or optionally substituted aralkyl; or

R<sup>3</sup> and R<sup>4</sup> together with the nitrogen to which they are attached form an optionally substituted 5- or 6- membered ring;

4. A compound according to any one of the preceding claims wherein M is nickel, chromium, copper, cobalt, zinc, iron, manganese or boron.

5. A compound according to any one of the preceding claims wherein M is nickel.

6. A compound according to any one of the preceding claims wherein Z is H and Y is CO<sub>2</sub>H or H.

7. A compound according to any one of the preceding claims wherein X is an electron withdrawing group.

8. A compound according to any one of the preceding claims wherein the value of (a+q+n) is 2 or 3.

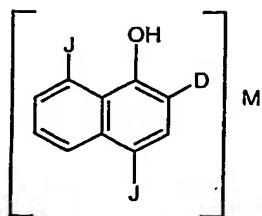


9. A compound according to any one of the preceding claims wherein J is of the Formula  $\text{SO}_2\text{NR}^6\text{R}^7$  wherein:

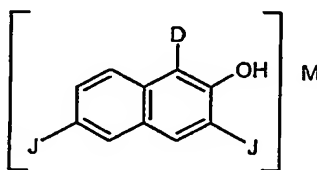
$\text{R}^6$  and  $\text{R}^7$  are each independently H, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted aralkyl; or

$\text{R}^6$  and  $\text{R}^7$  together with the nitrogen to which they are attached form an optionally substituted 5- or 6- membered ring.

10. A compound according to any one of the preceding claims of the Formula (5) or (6) or a salt thereof:



Formula (5)



Formula (6)

wherein:

D is an azotriazole group; and

M and J are as defined in claim 1.

11. A compound according to claim 10 wherein, J is  $\text{SO}_2\text{NR}^6\text{R}^7$  and one of  $\text{R}^6$  and  $\text{R}^7$  is H and the other is optionally substituted aryl.

12. A compound according to claim 10 wherein, J is  $\text{SO}_2\text{NR}^6\text{R}^7$  and one of  $\text{R}^6$  or  $\text{R}^7$  is H and the other is a 4-carboxy phenyl group.

13. A composition comprising:

- (a) one or more compound according to any one of the preceding claims; and
- (b) one or more water-soluble dye other than a compound according to any one of the preceding claims.

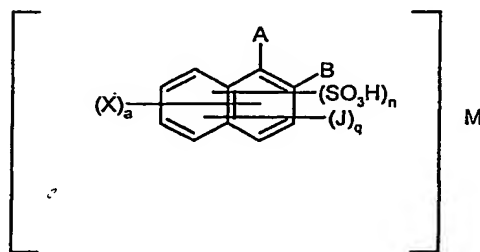
14. An ink comprising:

- (a) a compound according to any one of claims 1 to 12, or a composition according to claim 13; and
- (b) a liquid medium.

15. An ink comprising:
  - (a) a compound of the Formula (1) as defined in claim 1; and
  - (b) a liquid medium comprising a mixture of water and an organic solvent.
16. A process for printing an image on a substrate comprising applying thereto by means of an ink jet printer an ink containing a compound according to any one of claims 1 to 12 or a composition according to claim 13.
17. A substrate printed with an ink according to claim 14 or claim 15, or by means of the process according to claim 16.
18. An ink jet printer cartridge comprising a chamber and ink, wherein the ink is present in the chamber and the ink contains a compound according to any one of claims 1 to 12 or a composition according to claim 13.
19. An ink jet printer containing an ink jet printer cartridge, wherein the ink jet printer cartridge is as defined in claim 18.
20. A dye substantially as herein described with reference to any one of the examples.
21. An ink substantially as herein described with reference to any of the examples.

ABSTRACTCOMPOSITION, USE AND PROCESS

A metal chelate compound of the Formula (1) and salts thereof:



Formula (1)

wherein:

one of A and B is OH and the other is an azotriazole group;

each X independently is a substituent other than H, sulphonamido, carboxy, sulpho and carbonamido;

J is a sulphonamido group;

M is a metal or boron;

n and a are each independently 0, 1, 2, 3 or 4;

q is 1, 2, 3 or 4; and

(a+q+n) is 1, 2, 3 or 4.

Also claimed are compositions and inks containing a compound of Formula 1, a process for ink jet printing using the inks and an ink jet printer cartridge containing the ink.

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